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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(54) Title: THIN SELF-SUPPORTING INORGANIC GREEN COMPACTS AND PROCESS FOR THE PREPARATION OF SUCH GREEN COMPACTS

(57) Abstract

Thin self-supporting green compact, less than 25 μ thick, containing an inorganic substance and as a binder a polymer with a weight average molecular weight of more than 400,000, which polymer in a suitable solvent can form a thermoreversible gel above room temperature, the volume fraction of the inorganic substance being more than 45 % relative to the total amount of binder plus inorganic substance and a process to prepare such green compacts.

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THIN SELF-SUPPORTING INORGANIC GREEN COMPACTS AND PROCESS
FOR THE PREPARATION OF SUCH GREEN COMPACTS

The invention relates to a thin self-supporting inorganic green compact which contains an inorganic
5 substance and a binder and is less than 25 μm thick.
Such inorganic green compacts are described in EP-A-0210874.
A drawback of the green compacts described in said patent, in this case films, is that cellulose is used as
10 binder, which limits the stretchability of the green compacts. Because this means that the desired extremely thin films have to be produced in one go. The films are produced by first applying a thin layer of the solution containing binder and inorganic substance to a support, drying it and
15 then separating the layer from the support. Such a process imposes very high intrinsic requirements on the equipment to be used to produce the films because irregularities in thickness or cracks easily occur. For the same reason such processes are extremely sensitive to the occurrence in the
20 added inorganic substance of particles with dimensions similar to the layer thickness. In practice, it therefore appears to be hardly possible to produce very thin-walled objects without cracks in this manner, tests having shown that it is very difficult to remove the films from the
25 support, in particular in the case of thin films (10-20 μ). Moreover, cellulose is sensitive to moisture, as a result of which the dimensional stability is adversely affected, which precludes specific applications. In the framework of the invention reference is made to a green compact as long as
30 the organic binder is still present as such and has not yet been removed or converted.

The aim of the invention is to provide thin green compacts of an inorganic substance bound with an organic
5   binder which do not have the aforementioned drawbacks.

The green compacts according to the invention are characterized in that the binder consists substantially of a polymer with a weight average molecular weight of more than 400,000, which polymer, incorporated in a suitable solvent,
10 forms a thermoreversible gelling system with gel and dissolution points above room temperature, the volume fraction of the inorganic substance being more than 45% relative to the total amount of binder and inorganic substance.

15 Such green compacts are easily obtainable without having to impose particularly high requirements on the equipment to be used. Moreover, it is possible to use said green compacts to apply inorganic layers, whether or not sintered, in objects. An example of such an object is a
20 multilayer ceramic capacitor, in the case of which a low ceramic layer thickness is a great advantage with respect to the miniaturisation aimed at in this application.

The invention therefore also relates to a process for the preparation of said green compacts and the use of
25 the green compacts according to the invention in the application in objects of layers containing inorganic substance.

DE-A-2334704 describes the preparation of fibres of polyethylene oxide in which substantial amounts of fillers
30 can be incorporated. The polymer-solvent system described in said patent is a high-viscosity solution at room temperature, which causes problems with respect to the feeding of the extruder. Another drawback of the polyethylene oxide/water system used is that this system
35 does not form a gelling system until it is cooled to below room temperature. At room temperature the product obtained therefore remains tacky as long as it contains solvent. Consequently, the solvent has to be removed to enable further processing. This is a particular drawback because

the solvent has to be removed from the unstretched and thus
thicker green compact, which is more difficult and takes
5   longer.

Thermoreversible gelling systems are in the scope
of the invention understood to be systems characterized by
the fact that the conversion into a gel of a polymer
dissolved in a solvent is effected by means of a (rapid)
10 drop in temperature. Examples of thermoreversible gelling
systems with gel and dissolution points above room
temperature are: polyalkenes with the usual solvents such as
paraffins, toluene, xylene, tetralin or decalin; polyvinyl
alcohol (PVAL) with ethylene glycol as solvent;
15 polyacrylonitrile (PAN) with dimethylformamide as solvent,
to which zinc chloride is added as complexing salt, in an
amount of about 10 wt.% relative to the amount of PAN.

The green compact may have any simple shape
obtainable via the usual continuous shaping methods, such as
20 a fibre, film, or tube. The shape is not restricted to flat
objects. Three-dimensional structures such as curved films
or cylindrical shapes are also possible. If the green
compact concerns fibres the thickness of the green compact
is understood to be the diameter of the fibre.

25 The binder can be removed according to commonly
known methods, such as pyrolysis, extraction or firing. Good
results, particularly as regards dimensional stability, were
obtained by removing the binder by means of low-temperature
incineration with the aid of plasmas.

30 If so desired, the object may then be subjected to
sintering, in which case the object is brought to a certain
temperature for a certain amount of time, in a known manner.
The conditions to be applied are known in the literature and
depend on the inorganic substance used.

35 To obtain a continuous layer of inorganic material,
the filler content must be as high as possible. In the case
of the green compacts according to the invention the filler
content is more than 45 vol.%, usually 50-99 vol.% inorganic
substance relative to inorganic substance plus polymer

binder. In some cases it may be useful to use an inorganic substance with a bimodal particle size distribution to

5 obtain a high filler content.

By sintering the green compact after the removal of the binder a self-supporting, whether or not continuous, object can be obtained. As inorganic sinterable substances use may be made of all substances or mixtures that are

10 sinterable per se or of inorganic substances that are not sinterable per se, to which suitable sintering additives are added, for example SiO_2, Al_2O_3, $BaTiO_3$, Si_3N_4 mixed with Y_2O_3 or SiC mixed with boron compounds.

The green compacts appear to be suitable for many

15 applications. In some cases the green compact as such will meet the requirements, whereas in other cases the specific application will require a thin inorganic layer, which is obtained after the binder has been removed from the green compact, if so desired with subsequent sintering.

20 The following applications are illustrative as examples, but the list is not to be regarded as limitative.

If the inorganic substance has a high dielectric constant, thin dielectric layers can be obtained after firing and sintering, which are suitable for use in

25 capacitors. In addition, thin conductive films can be produced, so that multilayer ceramic capacitors in particular present good possibilities for the use of the green compacts according to the invention.

In addition, it appeared possible to produce very

30 thin substrata for hybrid electronic structures. Good results have been obtained in this field using Al_2O_3 as inorganic filler. An advantage of the green compact according to the invention in such applications is that the porosity of the green compact can be varied within wide

35 limits to meet the demands involved in the various applications.

The green films are suitable as thin flexible envelopes of objects for better protection from the influence of high-energy electromagnetic radiation. Several

metallic fillers can be considered for this purpose. The
green compacts are also very suitable for use as coatings.
5 Abrasion-resistant coatings can be applied to objects using,
for example, carbides or nitrides, in which case the
flexibility of the green compact appeared an advantage in
particular in obtaining a good cover for complex shapes. It
has been found that the green compact according to the
10 invention has sufficiently high strength and modulus to be
handled during the further processing. This is particularly
the case if the modulus of elasticity of the green compact
is at least 0.5 GPa.
        The invention also relates to a process for the
15 preparation of thin-walled inorganic green compacts. A
process for the production of filled fibres of organic
material is known from US-A-4411854, in which process a
high-molecular polyalkene with a weight average molecular
weight of more than 4×10^5 dissolved in a suitable solvent
20 with a binder content of less than 30 wt.%, relative to the
binder plus solvent, is converted, at a temperate above the
gelling temperature of the solution, into a fibrous,
solvent-containing object, which object is rapidly cooled to
below the gelling temperature and stretched. An additive was
25 added to the fibres to improve the tensile strength and the
modulus. It is advised to use less than 37.5% additive,
relative to the amount of polymer plus filler.
        It has now appeared possible to use the process
according to the invention to produce green compacts
30 containing very large amounts of inorganic substance, which
are dimensionally stable and stretchable and contain little
binder relative to the amount of inorganic substance. In
this manner a thin, continuous inorganic object can be
obtained after the removal of the polymer binder and,
35 optionally, sintering. Preferably, the green compact is
stretched biaxially because it has been found, surprisingly,
that the maximum possible draw ratio does not decrease when
the green compact is stretched biaxially. This is
particularly surprising because the maximum draw ratio does

decrease with an increasing filler content in the case of
uniaxial stretching. Another advantage is that the thickness
5   of the green compact decreases rapidly in biaxial
stretching, which means that thin stretched green compacts
can be easily obtained.

Preferably, use is made of a polymer with the
highest possible molecular weight. For it has been found
10 that if the molecular weight is high, the concentration of
polymer in solution may be low and will nevertheless, after
shaping, result in a coherent stretchable and dimensionally
stable structure. It is important to use the lowest possible
concentration of polymer binder in solution because then a
15 higher inorganic substance/polymer binder volumetric ratio
can be obtained after the removal of the solvent. This is
because the allowable amount of inorganic substance is
determined by the closest concentration of the particles in
the solution. For spherical particles of uniform size the
20 theoretical maximum amount of inorganic substance is thus 60
vol.% relative to inorganic substance plus polymer solution.
In practice, use will generally be made of amounts of
inorganic substance of between 20 and 40 vol.% in the
solution.
25   The filler content w of the green compact is
defined as:

$$w = V_i/(V_i + V_p) \tag{1}$$

The maximum possible filler content of the green compact
(w_{max}) is related to the filler content of the solution (a)
30 according to the equation:

$$w_{max}(a) = a/(a + M_{emelt}/M_n) \tag{2}$$

These quantities are defined as follows:

a $= V_i/(V_i + V_p + V_s)$, the filler content of the
35 solution;

V_p, V_i, V_s = the volume of the polymer, inorganic substance
and solvent, respectively;

M_{emelt} = the molecular weight of the polymer between two
cross-links in the equilibrium melt (g/mole)

M_n = the number average molecular weight of the
                 polymer (g/mole).

M_{emelt} can be determined according to the method described
in Advances in Polymer Science, 1974, part 16, Chapter 7.
The M_{emelt} to be determined for polyethylene in this manner
is 4000. M_n can be determined according to the usual
methods, for example GPC. The polydispersity defined as the
ratio of the weight average molecular weight and the number
average molecular weight depends on the molecular weight
distribution in the polymer and is between about 3 and 30 in
the case of the aforementioned polymers.
The maximum filler content of the green compact is
determined by the maximum filler content of the solution,
which, as already indicated above, is 0.6, according to
equation (1):

$$w_{max}(0.6) = 0.6/(0.6 + M_{emelt}/M_n) \qquad\qquad (3)$$

As an example, the values given in the $w_{max}(0.6)$
and $w_{max}(0.3)$ columns of Table 1 illustrate the ratios of
the weight average molecular weight M_w, the number average
molecular weight M_n and the maximum possible filler content
of the green compacts in the case of polyethylene, on the
basis of a polydispersity of 12, for a solution filler
content of 0.6 and 0.3, respectively.

T A B L E   1

M_w [g/mole]	M_n [g/mole]	$w_{max}(0.6)$ [-]	$w_{max}(0.3)$ [-]
120,000	10,000	0.6	0.42
480,000	40,000	0.85	0.75
960,000	80,000	0.92	0.85
1,200,000	100,000	0.93	0.88
2,400,000	200,000	0.97	0.94
6,000,000	500,000	0.99	0.97

Pr ferably, use is made of the finest possible
inorganic powder to obtain the smoothest possibl surface. A
5   good starting material can be obtained by suspending the
inorganic powder in a suitable medium. The polymer solvent
may be chosen as a suitable suspension medium. Surfactants
may be added to stabilize the suspension.
If so desired, the particle size can be reduced by
10   subsequent grinding, for example in a pebble mill, or via an
ultrasonic treatment.
Preferably, a volatile solvent is used. The use of
non-volatile solvents is described in US-A-3,926,851, where
the solvent is removed via extraction. Such a process is not
15   only time-consuming, but residual solvent and/or extracting
liquid are always retained in the end product, whereas only
negligible residues of the solvent used are retained in the
green compacts obtained with the process according to the
invention.
20   Preferably, the green compact obtained is subjected
to a relaxation step after cooling and stretching. After
such treatment the green compact retains its shape when
heated. Such a relaxation step may consist in heating the
green compact, for example under pressure, to above the
25   melting temperature of the binder for between 5 and 20
minutes and then cooling it, also under pressure. Such a
treatment can be very well combined with the lamination step
in the production of laminates.
It may be advantageous to subject the green compact
30   to irradiation, in particular electron irradiation, before,
during or after stretching, which results in products with
reduced creep. Moreover, it appears to be possible to
greatly shorten or even entirely omit the aforementioned
relaxation step after such irradiation.
35   In the process according to the invention varying
draw ratios may be used. Moreover, the green compact may be
stretched both biaxially and uniaxially. In the case of
uniaxial stretching the draw ratio will usually be more than
5x, whereas in the case of biaxial stretching the green

compact will be stretched at least 1.5x in longitudinal and
transverse direction, preferably betwe n 3 and 15x. It is
5   possible to use the same draw ratio in longitudinal and
transverse direction or to use a higher draw ratio in
longitudinal direction than in transverse direction or the
other way round. Longitudinal and transverse stretching may
be alternated, but are preferably done simultaneously, for
10 example in a simultaneous biaxial stretching unit. The
advantage of stretching in a simultaneous biaxial stretching
unit is that the film being stretched is clamped along its
edges, which means that the film surface is free from
equipment surfaces, whereas stretching done with rolls may
15 easily cause tear formation or an uneven thickness due to
irregularities in the surface of the rolls or due to the
occurrence of relatively large inorganic dust particles.

The present process is based on the use of
combinations of a high-molecular polymer and a solvent,
20 which combinations form thermoreversible systems. Polyvinyl
alcohol or high-molecular linear polyalkenes, such as
polyethylene, polypropylene and/or mixtures or copolymers
hereof are suitable for use as polymer. The polymers may
contain the usual additives such as stabilizers, colourants,
25 pigments, etc.

Extremely suitable are solutions of linear
polyethylene with a weight average molecular weight of at
least 4×10^5 g/mole, preferably of at least 8×10^5 g/mole.
High-molecular linear polyethylene is understood to be
30 polyethylene that may contain minor amounts, preferably at
most 5 mol.%, of one or more copolymerised other alkenes
such as propylene, butylene, pentene, hexene,
4-methylpentene, octene, etc. The polyethylene may contain
minor amounts, for example at most 25 wt.%, of one or more
35 other polymers, in particular an alkene-1-polymer such as
polypropylene, polybutylene or a copolymer of propylene and
a minor amount of ethylene.

Preferably, use is made of a polymer with a narrow
molecular weight distribution, for example with a weight

average molecular weight and number average molecular weight
ratio of less than 10, preferably 5. The advantage that can
5   thus be obtained is that a relatively larger amount of
solvent may be used at the same average molecular weight.
The weight average molecular weight can be determined
according to known methods by gel permeation chromatography
and light scattering.
10   The concentration of polymer in the solution may
vary, dependent in part on the nature of the solvent and the
molecular weight of the polymer.
            Solutions with a polymer concentration of more than
60 wt.%, relative to the amount of polymer plus solvent, are
15   rather difficult to handle on account of their high
viscosity, in particular when use is made of polymer with a
very high molecular weight, for example of more than 1 x
10^6 g/mole. In general, use will therefore be made of a
polyalkene solution with a concentration of between 0.5 and
20   40 wt.%, in particular of between 2 and 20 wt.%.
            The conversion of the solution into a green compact
can be effected in various manners, for example by extrusion
via a spinneret or a flat-sheet or plate die. Of course, it
is also possible to cast the solution onto, for example, a
25   tape or roll, roll or calender it. In the preparation of
films and the like the solution is preferably cast onto a
tape or the like if the polymer concentration is fairly low,
whereas it is preferably extruded directly in the case of a
high concentration.
30   In the case of spinning for example, the
temperature of the solution is preferably at least 100°C and
more in particular at least 120°C, and the boiling point of
the solvent is preferably at least 100°C and in particular
at least the same as the conversion or spinning temperature.
35   The boiling point of the solvent must not be so high that it
becomes difficult to evaporate it from the intermediates
obtained because in that case an extraction step will be
required.
            The conversion temperature and the dissolution

temperature must not be so high as to cause substantial
thermal decomposition of the polymer. For this reason these

5 temperatures will usually be chosen below 240°C.

The product obtained is cooled to below the gelling
point of the solution. This can be effected in any suitable
manner, for example by passing the product through a liquid
bath or through a chimney. When cooled to below the gel

10 point of the polymer solution, the polymer forms a gel. An
object consisting of this polymer gel has sufficient
mechanical strength to be processed further, for example via
the commonly used conveyors, rolls, etc.

The gel thus obtained is then stretched. This gel
15 may still contain substantial amounts of solvent, up to
amounts that are hardly lower than those contained in the
original polymer solution. It is also possible to remove a
portion of the solvent, or even substantially all of the
solvent, from the gel before the stretching, for example by

20 evaporation or by washing it out with an extracting liquid.

The possibility of varying the amount of solvent
present after gelling without affecting the essence of the
stretchability leads to great flexibility in the control of
the characteristics of the end product. Preferably, use is

25 made of more than 10 wt.% solvent relative to the total
weight of polymer and solvent. The green compact obtained in
this manner is characterized by better mechanical
properties, such as lower porosity, good workability and a
modulus of elasticity of > 0.5 GPa.

30 It is also possible to use the amount of solvent
still present during stretching to control the porosity of
the end product, in particular if use is made of a solvent
that is removed after the stretching step. By using a
solvent that can be removed during stretching different

35 effects can be combined.

Preferably, the gels are stretched at elevated
temperature, in particular at a temperature of over 75°C.
The gels can be brought to the stretching temperature by
passing them through a zone with a gaseous or liquid medium

that is maintained at the required temperature. A chimney
with air as gaseous medium is very suitable but it is also
5   possible to use a liquid bath or any other suitable device.
        In stretching, (any) residual solvent will be
separated from the product. Preferably, this is stimulated
with the aid of suitable methods, for example by removing
the solvent vapour by passing a hot gas or air stream over
10 the product in the stretching zone or by stretching in a
liquid bath containing a medium that extracts the solvent.
The green compact ultimately obtained must be free of
solvent and the conditions are with advantage chosen so that
this state is already reached, or is at least virtually
15 reached, in the stretching zone.
        The density of the green compact (ρ_{exp}) is
determined by dividing the weight of a specimen by the total
macroscopic volume as obtained, for example, via length x
width x thickness. The theoretical maximum density (ρ_{theor})
20 is determined from the known densities of the individual
constituent components. The total porosity (%) of the green
compact follows from the ratio of the theoretical and the
experimental density: porosity = (ρ_{exp}/ρ_{theor}) x 100%.
        Mechanical properties are determined from
25 stress/strain curves obtained at room temperature with the
aid of a tensile strength tester. Specimens measuring 15 x
170 mm are stretched at a speed of 100%/minute. The modulus
(E) follows from the maximum of the first derivative of the
stress/strain curve. Both the modulus and the tensile
30 strength (T) are relative to the original cross-sectional
area of the samples; the material properties are calculated
by multiplying by a factor of 100/(100-porosity). The
elongation at break is defined as the elongated length at
the point of rupture divided by the initial length.
35   The invention is further illustrated with the aid
of the following examples without, however, being limited
thereto.
        The concentration of inorganic substance given in
Tables 2 through 5 is the filler content w, calculated

according to formula (1). The concentration ∅ was calculated
as the polymer/ polymer plus solvent volumetric ratio.

5

Example 1

        10 parts by volume of polyethylene ($M_w \sim 2 \times 10^6$
g/mole) were added to 30 parts by volume of Decalin, after
which the suspension obtained was degassed in a vacuum oven.

10 Then 30 parts by volume of Al_2O_3 (and a small amount of
surfactant) were added to 60 parts by volume of Decalin and
the suspension obtained was ground in a pebble mill for 72
hours. After degassing and grinding the aforementioned
suspensions were mixed in a 1 : 1 ratio so that finally a

15 suspension was obtained with a polymer : solvent : Al_2O_3
volumetric ratio of 10 : 90 : 30 (p : s : i). The suspension
obtained was fed to a twin screw extruder equipped with a
spinning pump, a Sulzer mixer and a flat-sheet die and was
processed at about 170°C. After extrusion the film obtained

20 was quenched in water and partially dried. Then the film
obtained was biaxially stretched at 125°C and a draw ratio
of 10 x 10 and was heated to 170°C for 7 minutes in a press,
at a pressure of about 100 kg/cm^2. The film obtained was
about 15 μm thick.

25

Example 2

        The process of example 1 was repeated, but the
molecular weight, the concentration of the polymer in the
solvent and the total amount of inorganic substance were

30 varied according to the data shown in Table 2. In tests a
and b polyethylene with a relatively low molecular weight
was used. The films obtained could not be stretched
homogeneously. The maximum biaxial draw ratio was low.

T A B L E   2

No	Mw (g/mole)	suspension p : s : i	Ø [-]	w [-]	λ_{biax} [-]	thickness [μm]
1)	8.3×10^5	35:65:30	0.35	0.46	5x5	24
2)	8.3×10^5	35:65:30	0.35	0.46	10x10	8
3)	8.3×10^5	15:81:20	0.15	0.57	5x5	13
4)	8.3×10^5	15:81:20	0.15	0.57	10x10	6
5)	2×10^6	20:80:20	0.20	0.50	5x5	12
6)	2×10^6	20:80:20	0.20	0.50	10x10	4
7)	2×10^6	10:90:30	0.10	0.75	5x5	14
8)	2×10^6	5:95:20	0.05	0.80	5x5	8
9)	5×10^6	10:90:20	0.10	0.67	5x5	10
a)	2×10^5	50:50:30	0.50	0.375	–	–
b)	2×10^5	30:70:30	0.30	0.50	–	–

Example 3

Suspensions were prepared in the same manner as in
example 1. The suspension was heated with stirring to 160°C
in an erlenmeyer flask in a silicone bath. The stirring was
stopped after the Weisenberg effect. After having been
maintained at 160°C for about 2 hours, the polyethylene
solution containing the suspended inorganic filler was
poured into an aluminium dish. After the complete or partial
evaporation of the solvent a filled film was obtained, which
was stretched and relaxed in the same manner as in example
1. The data relative to the filler content of the polymer,
the concentration of polymer in the solvent and the
inorganic substance content were varied as shown in Table 3.
Experiments a and b refer to polyethylene with a relatively
low molecular weight. The films obtained were brittle.

T A B L E 3

No	Mw (g/mole)	suspension p : s : i	Ø [-]	w [inorg.]	λ_{biax} [-]	thickness [μm]
a)	2×10^5	10:90:30	0.10	0.75	–	–
b)	3×10^5	10:90:30	0.10	0.75	–	–
1)	2×10^6	2:48:20	0.04	0.91	10x10	9
2)	5×10^6	2:98:20	0.02	0.91	10x10	6
3)	5×10^6	1:99:20	0.01	0.95	10x10	8

Example 4

Films were prepared according to example 3. The films were stretched both biaxially and uniaxially. Uniaxial stretching was done with the aid of a shoe, at 130°C. The draw ratio was determined with the aid of marks. Biaxial stretching was done according to example 1. The concentration of polymer in solvent, the filler content and the draw ratio (biaxal and uniaxial) were varied while the molecular weight of the polymer remained unchanged. Table 4 shows the maximum uniaxial draw ratio (λ_{uniax}) at different filler contents. λ_{uniax} appeared to decrease considerably at high filler contents. At all filler contents a minimum biaxial draw ratio of 10x10 appeared feasible. The maximum possible biaxial draw ratio could not be determined due to equipment limitations.

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T A B L E   4

No	Mw (g/mole)	suspension p : s : i	Ø [-]	w [-]	λ_{uniax} [-]	λ_{biax} [-]
1)	2×10^6	2:98:0	0.02	0	110	10x10
2)	2×10^6	2:98:0.2	0.02	0.10	120	10x10
3)	2×10^6	2:98:0.5	0.02	0.20	105	10x10
4)	2×10^6	2:98:1	0.02	0.35	90	10x10
5)	2×10^6	2:98:2	0.02	0.50	50	10x10
6)	2×10^6	2:98:4.7	0.02	0.70	14	10x10

Example 5

Polypropylene was processed in the same manner as in example 1. The data are shown in Table 5.

T A B L E   5

No	Mw (g/mole)	suspension p : s : i	Ø [-]	w [-]	λ_{biax} [-]	thickness [μm]
1)	1.5×10^6	10:90:20	0.10	0.67	5x5	13
2)	1.5×10^6	5:95:30	0.05	0.86	5x5	8

Example 6

The process of example 1 was repeated, on the understanding that use was made of barium titanate powder and that no relaxation step was carried out. The amounts were adjusted so that finally a suspension was obtained with a polymer : solvent : barium titanate ratio of 10 : 90 : 11 (p : s : i). Parts of the film obtained were partly dried at room temperature for varying lengths of time, after which

they were biaxially stretched at a draw ratio of 4 x 4. The
amount of solvent still pr sent at the beginning of the
stretching procedure was determined gravimetrically.

The mechanical properties and porosities of the
resulting green compacts were compared. The green compacts
obtained in tests 5 and 6 appeared to be self-supporting,
but difficult to handle, due largely to their great
sensitivity to electrostatic charging. The results are shown
in Table 6. These results show, among other things, that the
porosity can be varied within wide limits.

T A B L E 6

Test No.	[Dec]*	elongation at break	E	T	Porosity
	%	%	GPa	GPa	%
1	38	> 100	0.80	0.06	43
2	29	> 100	1.10	0.06	52
3	20	60	0.62	0.06	74
4	10	30	0.56	0.07	80
5	1	30	0.34	0.05	82
6	0	30	0.22	0.04	86

[Dec] is the weight percentage of decalin at the beginning
of the stretching procedure, calculated on the basis of the
total amount of polymer plus solvent.

Example 7

Polyethylene ($M_w \approx 2.0 \times 10^6$ g/mole), decalin and
barium titanate (Type X7R302H of TAM[R], Buffalo, NY, USA)
were used to prepare suspensions according to the process of
example 1, with p:s:i volumetric ratios of 10:90:15.3 and
10:90:23.5, which suspensions were extruded to obtain films.
The films were biaxially stretched into 20-μm thick films,

at a draw ratio of 4.5 x 4.5. Ten layers of the stretched
film were placed on top of each other and compressed for 30
5   minutes at 180°C and a pressure of 10 MPa. The compressed
laminates were subsequently fired at 550°C, in a nitrogen
atmosphere, and sintered for 2 hours at 1300°C. No bending
or non uniform shape changes where observed upon binder
burn-out and firing. After each of the described steps the
10 density of the samples was determined as a percentage of the
density of the barium titanate. The results are given in
Table 7.

T A B L E   7

15

			density/5.89 x 100%			
sample	p:s:i	vol.%	green compact	after compression	after firing	after sintering

20

1	10:90:16.3	60	33	59	61	96
2	10:90:16.3	60	34	52	52	96
3	10:90:23.5	70	41	57	67	99

25

The relative dielectric constant of sample 3, determined at
25°C and 1 kHz, was 3300, which agrees with the value
specified by the supplier for the starting material.

30

Example 8

The process of example 1 was repeated, but instead
of Al_2O_3 use was made of barium titanate in a p:s:i
volumetric ratio of 10:90:11. Samples of the film obtained
35 were subjected to biaxial stretching either immediately,
that is, without drying, or after drying, in which cases the
decalin content was 37 wt.% and < 4 wt.%, respectively.
After stretching, the samples were compressed as in example
1. The results are summarized in Table 8.

T A B L E   8

before compression							after compression	
draw ratio	elonga- tion at break %	tensile strength GPa	modu- lus of elas- ticity GPa	dens. g/ml	thick- ness μm	poros. %	thick- ness μm	poros. %

not dried:

3*3	201	0.041	0.71	2.29	45	40	29	5
3*4	240	0.052	0.70	1.98	33	48	19	6
3*4.5	200	0.060	0.90	2.18	30	43	18	4

dried:

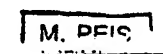|								
5.5*5.5	31	0.036	0.21	0.53	84	86	24	15

-20-
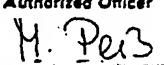
C L A I M S

5   1. Thin self-supporting green compact that contains an
        inorganic substance and a binder and is less than 25 μm
        thick, characterized in that the binder consists
        substantially of a polymer with a weight average
        molecular weight of more than 400,000, which polymer
10   incorporated in a suitable solvent forms a
        thermoreversible gelling system with gelling and
        dissolution points above room temperature, the volume
        fraction of inorganic substance being more than 45%
        relative to the total amount of binder plus inorganic
15   substance.
    2. Green compact according to claim 1, characterized in
        that the volume fraction of inorganic substance is less
        than or equals $0.6/(0.6 + M_{emelt}/M_n)$, M_{emelt} being the
        molecular weight of the polymer between two cross-links
20   in the equilibrium melt and M_n being the number average
        molecular weight of the polymer.
    3. Green compact according to claim 1 or 2, characterized
        in that the polymer is a polyolefin.
    4. Green compact according to claim 1 or 2, characterized
25   in that the polymer is a polyvinyl alcohol.
    5. Green compact according any one of claims 1-4,
        characterized in that the green compact is obtained via
        biaxial stretching.
    6. Green compact according to any one of claims 1-5,
30   characterized in that the porosity is less than 80%.
    7. Green compact according to any one of claims 1-6,
        characterized in that the modulus exceeds 0.5 GPa.
    8. Green compact according to any one of claims 1-7,
        characterized in that the ratio of the weight average
35   and the number average molecular weight is less than 10.
    9. Green compact according to any one of claims 1-8,
        characterized in that the inorganic substance is
        sinterable.

10. Process for the preparation of thin-walled inorganic green compacts containing sinterable inorganic substances and a high-molecular binder with a weight average molecular weight of more than 4×10^5, in which the binder dissolved in a suitable solvent, the concentration of the binder being less than 60 wt.% relative to the binder plus solvent, is converted into a solvent-containing intermediate at a temperature above the gelling temperature of the solution, said intermediate is rapidly cooled to below the gelling temperature to form objects and is stretched before, during or after the gelling, whether or not in the presence of the solvent, characterized in that the solvent-containing green compact is formed by adding an inorganic substance, in an amount of more than 45 vol.% relative to the total volume of binder plus inorganic substance.

11. Process according to claim 10, characterized in that a volatile solvent is used.

12. Process according to claim 10 or 11, characterized in that the green compact is stretched biaxially.

13. Process according to claim 12, characterized in that when the stretching is started the green compact still contains at least 10 wt.% solvent, relative to the total amount of solvent plus binder.

14. Process according to any one of claims 10-13, characterized in that the green compact obtained is subjected to a relaxation step.

15. Use of green compacts according to any one of claims 1-9 for the application in objects of layers containing inorganic substance.

16. Green compact as described and illustrated with the aid of the examples.

17. Process as described and illustrated with the aid of the examples.

18. Application as described and illustrated with the aid of the examples.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION F SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 08 K 3/00, C 04 B 35/00, C 04 B 38/06.

II. FIELDS SEARCHED

Minimum Documentation Searched

Classification System	Classification Symbols
IPC[5]	C 08 K, C 04 B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP, A, 0210874 (THE DOW CHEMICAL COMPANY) 4 February 1987 see the whole document (cited in the application)	1-18
A	Database Derwent World Patent Index, AN 86-016951 03 & JP, A, 60239352 (HITACHI CHEMICAL K.K.) 28 November 1985 see the abstract	1,10
A	EP, A, 0227037 (MITSUI TOATSU CHEMICALS INC.) 1 July 1987 see claims 1-5	1,3,5,10, 12
A	EP, A, 0206040 (HOECHST AG) 30 December 1986 see claims 1-3,10	1,3,5,10,12

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the International filing date but later than the priority date claimed

"T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
23rd October 1990	14. 11. 90

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	M. Peis M. PEIS

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